

Plasmonic Gold Nanostars Incorporated into High-Efficiency Perovskite Solar Cells

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Incorporating appropriate plasmonic nanostructures into photovoltaic (PV) systems is of great utility for enhancing photon absorption and thus improving device performance. Herein, the successful integration of plasmonic gold nanostars (AuNSs) into mesoporous TiO₂ photoelectrodes for perovskite solar cells (PSCs) is reported. The PSCs fabricated with TiO₂-AuNSs photoelectrodes exhibited a device efficiency of up to 17.72%, while the control cells without AuNSs showed a maximum efficiency of 15.19%. We attribute the origin of increased device performance to enhanced light absorption and suppressed charge recombination.

Perovskite solar cells (PSCs) have recently attracted considerable research interest with dramatic increases in efficiencies reported in the past few years.^[1, 2] A certified power conversion efficiency (PCE) for PSCs of 22.1% has been demonstrated and this is expected to exceed 30%.^[3, 4] In addition to their success in research, PSCs have become commercially attractive owing to the potential of delivering remarkably high PCEs with low production costs.^[5] High performing PSCs are no longer limited to small active areas (<0.1 cm²). The commercialization of PSCs is becoming increasingly more attractive based on recent success in large-area highly-efficient PSCs.^[6]

In general, the most efficient PSCs rely on a mesoporous structured thin film of TiO₂ as an electron transporting layer (ETL) due to its high optical transparency and well-defined band alignment.^[7, 8] However, due to the thin layer of TiO₂, a large portion of light passes through the conventional films limiting device performance. Therefore, further improvements in the PV efficiency of PSCs are likely to be achieved through optical management.

One promising strategy is to utilize plasmonic nanostructures that can enhance the light harvesting efficiency (LHE) and/or reduce the exciton binding energy of the PV devices.^[9] Moreover, recent study reported the evidence of the electron transfer between perovskite and gold nanoparticle (AuNP) based plasmon resonance scattering.^[10] Since the size and shape of

metallic nanostructures play a critical role in achieving panchromatic photon absorption, spherical nanoparticles and nanorods of gold and silver have been previously used in PSCs.^[11-15] Although these plasmonic nanostructures have shown some promise in efficiency enhancement of PSCs, complex nanostructures such as nanostars are of great interest due to their highly concentrated field intensity around the branched corners and edges to enhance the LHE. However, until now, there have been no effort on the use of plasmonic gold nanostars (AuNSs) incorporated in PSCs.

Herein we report high efficiency PSCs employing AuNSs incorporated mesoporous TiO₂ electron-transporting layer (Figure 1a). For comparison, we also fabricated PSC devices based on AuNPs and gold nanorods (AuNRs) incorporated into TiO₂ films. A broadband quantum efficiency enhancement in the PSCs was observed by introducing AuNSs into the mesoporous TiO₂ photoelectrodes. As a result, the TiO₂-AuNS photoelectrode based PSC displayed the highest PCE of up to 17.72% while the control device with TiO₂-only showed a maximum efficiency of 15.19%.

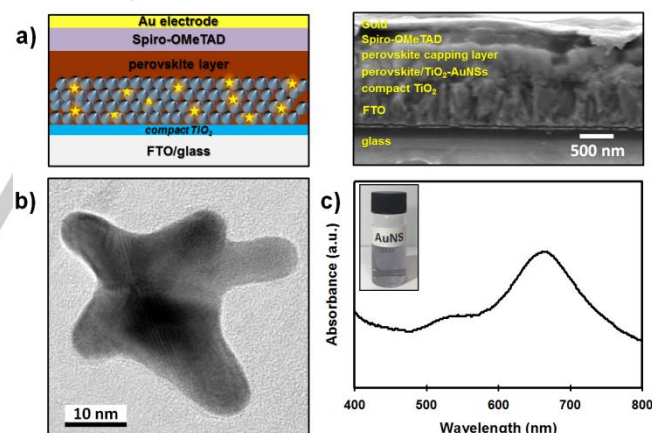


Figure 1. (a) Schematic illustration (left) and cross sectional scanning electron microscopy (SEM) image (right) of PSC device employing AuNSs in the mesoporous TiO₂. (b) TEM image and (c) UV-vis spectra of AuNSs.

The high-resolution transmission electron microscopy (TEM) image in Figure 1b shows that the as-prepared AuNSs, with a size of around 20-30 nm, contain multiple well-defined pods/tips on the surface. Figure 1c shows the UV-vis absorption spectra of AuNSs dispersed in water. The appearance of the strong resonance band of AuNSs centered at a long wavelength of > 650 nm is due to the formation of tips, while the shoulder at ~530-550 nm is associated with the transverse plasmon mode of the cores.^[16] Such AuNSs are expected to have strong local electromagnetic field enhancement around the pods/tips and also provide excellent light scattering,^[16, 17] which will lead to an enhancement in LHE of the devices. To verify the presence of the AuNSs in the mesoporous TiO₂, the photoelectrodes were

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characterized using X-ray photoelectron spectroscopy (XPS). Figure S1 in the supporting information shows the Ti2p (a) and Au4f spectra (b). A monatomic XPS depth profile was performed to confirm the Au nanostructures were within the mesoporous TiO₂ layer. The binding energy was measured to be 84.0 eV for Au4f (7/2) and 87.5 eV for Au4f (5/2), where the Au4f region shows a spin-orbit component of 3.5 eV and asymmetric peak shapes confirming the presence of AuNSs.

PSCs with and without AuNSs in the TiO₂ photoelectrodes were fabricated and tested using simulated AM1.5 sunlight with an output power of 100 mW cm⁻². The average PV efficiency of the cells increased from ~14.50% (without AuNSs) to ~16.90% after adding AuNSs into the films. As shown in Figure 2a, the PV efficiencies of both devices with and without AuNSs were highly reproducible, suggesting that the addition of AuNSs in the mesoporous TiO₂ layer does not alter the device reproducibility. The photocurrent density-voltage (*J*-*V*) characteristics of the best devices based on both TiO₂-only and TiO₂-AuNS photoelectrodes are displayed in Figure 2b and the corresponding PV parameters are given in the inset. The measured short-circuit current (*J*_{sc}), open-circuit voltage (*V*_{oc}), and fill factor (*FF*) values for the device with the AuNSs were 22.97 mA cm⁻², 1.08 V, and 0.71, respectively, yielding a PCE of 17.72%, which was higher than that (15.19%) of the TiO₂-only based cell. For comparison, we also fabricated PSCs based on the AuNPs and AuNRs incorporated TiO₂ photoelectrodes and tested their performances under the same conditions (Figure S2).

Some recent studies showed that the incorporation of both AuNPs and AuNRs can significantly improve the PV efficiencies of the PSCs due to the enhanced LHE and/or reduced the exciton binding energy of the light absorber in the devices.^[11-13] Interestingly, Figure S3 and Table S1 (supporting information) show that although all plasmonic nanostructures incorporated devices showed improved efficiencies, the addition of AuNSs was the most effective plasmonic nanostructure and exhibited a 2.5 % absolute (or 14.30% relative) enhancement in the PCE as compared to the control cell. We note that the achieved PCE (17.72%) using our TiO₂-AuNS photoelectrode based device is higher than other reported values of the PSCs based on plasmonic nanostructures.^[11-15, 18]

Compared with AuNPs and AuNRs, AuNSs are unique in their structure which consists of a central core with multi-branched (tips) surface.^[17] These unique nanostructures result in a well-defined double localized surface plasmon resonance (LSPR) peaks at 495-560 nm (core) and 650-680 nm (multi-branched tips) (see Figure S2d), which are expected to lead to strong local electromagnetic field enhancement around the branched tips and also an improved light scattering effect.^[16] Therefore, the improved efficiency for structures using AuNSs in comparison to the other nanoparticles can be attributed to a better overlap between the LSPR excitation wavelengths in collaboration with the mixed perovskite absorber combined with localized field enhancement due to the jagged structures.

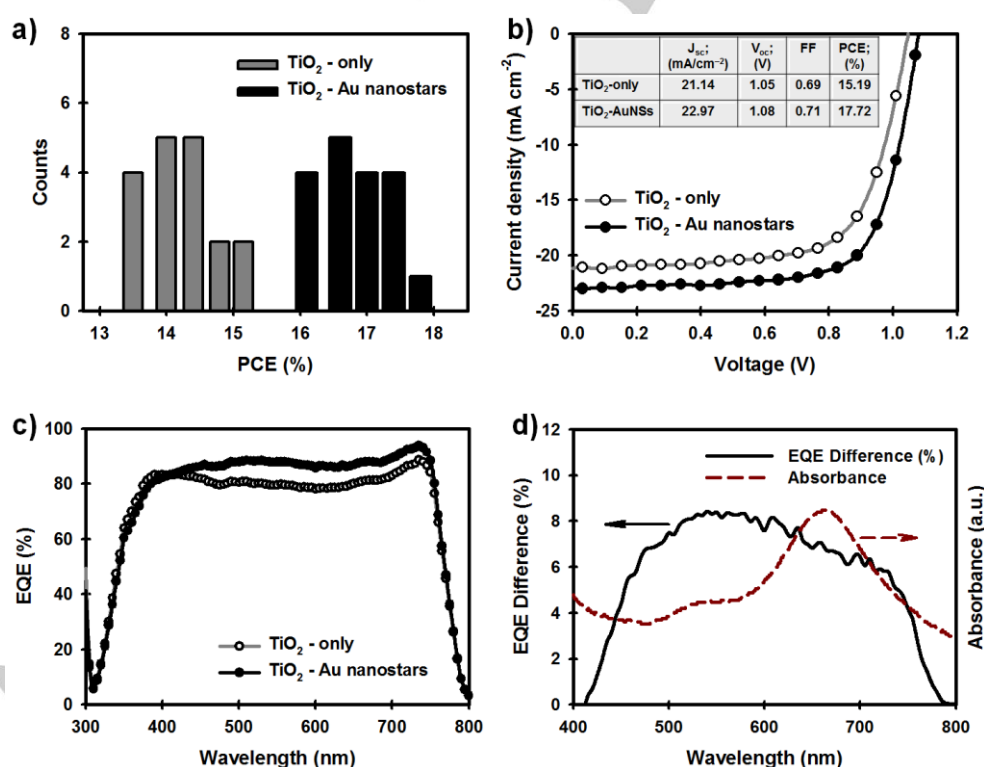


Figure 2. (a) Histogram of the PCE of devices (calculated based on 18 individual cells), (b) *J*-*V* curves and (c) EQE spectra of the best-performance cells fabricated with and without AuNSs in the photoelectrodes. (d) The increase in EQE (EQE difference), with the addition of AuNSs, overlapped with the UV-vis absorption spectrum of AuNSs.

To confirm the J_{sc} enhancement of the devices after adding AuNSs, the external quantum efficiencies (EQE) of the PSCs with and without AuNSs were measured (Figure 2c). The calculated J_{sc} values from integration of the EQE spectra for the TiO_2 -only and TiO_2 -AuNSs electrodes based PSCs were 20.41 and 22.10 mA cm^{-2} , which are in good agreement with the observed J_{sc} in the J - V characteristics. The PSC with AuNSs in the photoelectrode exhibited a clear improvement in the EQE value from around 440 to 750 nm compared to the control cell. To understand the origin of the J_{sc} enhancement after adding AuNSs into the TiO_2 layer of PSCs, we further calculated the increase in the EQE (EQE difference) and also plotted the UV-vis spectrum of AuNSs (see Figure 2d). The highest enhancement in EQE was found to be present at ~520–530 nm and corresponded to an EQE improvement of 8%, supporting the increase in J_{sc} . A broad core peak between 495–560 nm clearly covers the 520–530 nm region on the EQE.

Another PV parameter that has an influence on the efficiency of the PSCs after adding AuNSs was the improved FF . To investigate the charge transfer and recombination properties of the devices, electrochemical impedance spectroscopy (EIS) was used and these results are shown in Figure 3a. It is well understood that the small arc at the high frequency region is associated with the charge-transfer resistance (R_{ct}) at the counter electrode of the devices, while the main arc low frequencies is attributed to the charge recombination resistance (R_{rec}). Notably, there was no significant difference in the R_{ct} (~400 Ω) of the devices with and without AuNSs. Interestingly, the R_{rec} (3.07 k Ω) of the TiO_2 -AuNS photoelectrode based device was higher than that (2.65 k Ω) of the control device, indicating that the addition of AuNSs into the TiO_2 suppressed the recombination rate of the devices. Such improvements in the R_{rec} after adding plasmonic nanostructures have also been observed in recent studies.^[14, 19] According to these studies, the suppressed recombination of the devices after adding AuNSs into the TiO_2 photoelectrodes can be associated with the following factors: (i) better pore-filling of the perovskite into the TiO_2 -AuNSs film, as compared to the TiO_2 -only film,^[14] (ii) the electron-hole separation centers, formed by the Schottky barrier at the Au/ TiO_2 interface, is beneficial in improving the movement of photogenerated electrons shuttling through the porous TiO_2 ,^[20] and (iii) fast charge extraction and transport caused by the reduced of exciton binding energy of the perovskite.^[12]

Dark J - V measurements of the devices were carried out to further study the charge recombination properties (see Figure 3b). Saturation-current (J_{sat}) values and ideality factors of the devices fabricated with and without AuNSs were obtained and compared. Notably, both lower J_{sat} and ideality factors indicate less charge recombination from reverse current and charge trapping is occurring in the diode with AuNSs present.^[21, 22] The J_{sat} ($5.15 \times 10^{-10} \text{ mA cm}^{-2}$) of the TiO_2 -AuNS photoelectrode based cell was 2.5 times lower than that ($1.29 \times 10^{-9} \text{ mA cm}^{-2}$) of the control device. Moreover, the ideality factor of the device with the AuNSs was 1.54, which was lower than that (1.63) of the control cell.

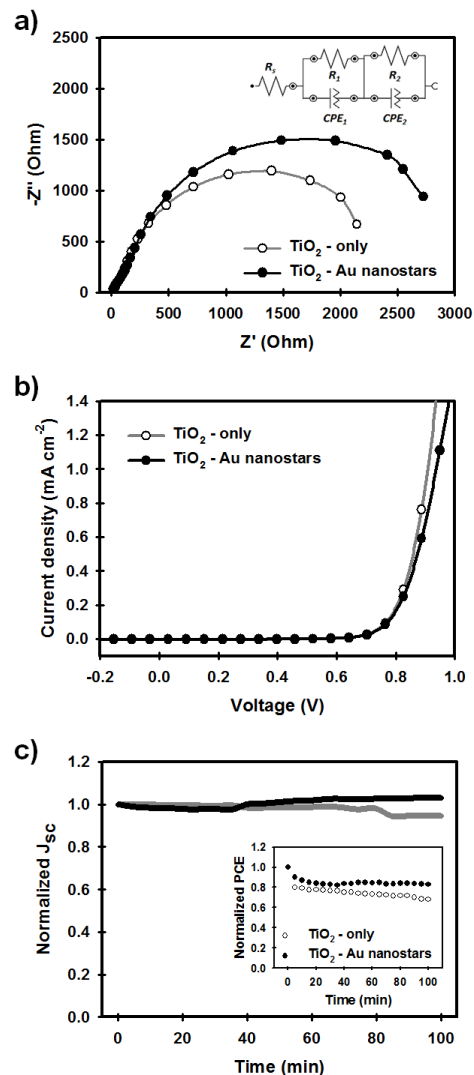


Figure 3. (a) Nyquist plots of EIS measurements (measured under illumination at 0.8 V bias, (b) dark J - V curves, and (c) Normalized J_{sc} values and PCEs (inset) of the devices as a function of time exposed to continuous light illumination (100 mW cm^{-2} , Xe lamp).

In addition to achieving high efficiency PSCs, the stability is one of the most important barriers to commercialization of PSCs. The photostability of the unencapsulated devices with and without AuNSs in the photoelectrodes, displayed in Figure 3c, was tested by exposing cells to continuous light illumination. Interestingly, the J_{sc} of the TiO_2 -AuNS photoelectrode based device was more stable, as compared to the control cell, over 100 min light exposure. Due to this stable J_{sc} value, the device fabricated with AuNSs retained ~83% of its initial PCE after 100 min of irradiation, while the control cell preserved ~68%. This improved photostability of the TiO_2 -AuNSs photoelectrode based device could be due to the fact that the metallic AuNSs are expected to help more even heat dissipation throughout the TiO_2 during irradiation. Additionally the heat generated during the light soaking could lead to minor re-crystallization or rearrangements in the solid. In the present situation where there are "foreign" objects in the solid, such small reorganizations could lead to

better connections between components of the solid yielding better efficiency.

Hysteresis behavior of our devices was investigated by scanning the *J-V* characteristics of the cells using different scan directions (reverse and forward) (Figure S4). There was no significant change in the device hysteresis behavior before and after adding AuNSs.

In summary, we have successfully designed an efficient ETL by incorporating mesoporous TiO₂ nanoparticles and star-shaped Au nanostructures for PSCs. This unique ETL based PSC device delivered a PCE of up to 17.72% which is significantly higher than that (15.19%) of the control device fabricated without plasmonic structures. The enhanced PV performance of the PSCs with TiO₂-AuNSs photoelectrodes originates from the enhanced LHE and suppressed charge recombination rate of the devices by adding AuNSs.

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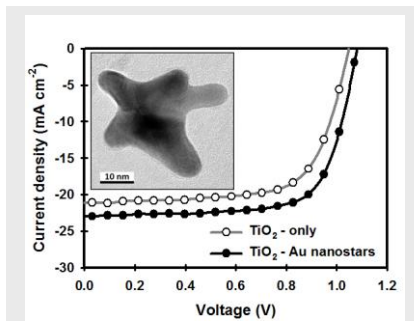
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COMMUNICATION

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